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GaInNAs Material Properties for Long Wavelength Opto-Electronic Devices

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ABSTRACT

Dilute nitrogen GaInNAs is a new promising material as an active region for use in 1.3 and 1.55 μm opto-electronic devices. It has been commonly observed that increasing the nitrogen content generally reduces the optical emission intensity and increases laser threshold. However, some non-radiative recombination defects are removed from the material during a post-growth anneal. One drawback to the anneal is that nitrogen out-diffuses from the quantum wells and blue-shifts optical emission. Using a modified active region structure, we have decreased nitrogen out-diffusion and reduced the luminescence blue-shift while still improving crystal quality. The growth consists of high nitrogen GaNAs barriers grown between lower nitrogen GaInNAs quantum wells. As an added benefit, the nitride barriers strain compensate for the compression in the high In content GaInNAs wells. Furthermore, in order to improve luminescence at long wavelengths, we have added Sb to GaInNAs and have observed high intensity photoluminescence (PL) out to 1.6 μm . We have grown and fabricated in-plane GaInNAs lasers that emit at 1.3 μm with a current threshold density of 1.2 kA/cm^2 and GaInNAsSb lasers with emissions at 1.46 μm with a current threshold of 2.8 kA/cm^2 .

INTRODUCTION

There currently is a high demand for low cost 1.3-1.55 μm diode lasers that can operate over a significant temperature range (-10 to 85°C) with moderate power (>10 mW). There are many applications for light sources in this wavelength region including telecommunication lasers, modulators and amplifiers. Current solutions based on InP have serious limitations covering the entire 1.3-1.55 μm wavelength range [1]. The GaInNAs alloy grown on GaAs has been predicted to extend over that wavelength range with several material advantages. Due to a large bandgap bowing, small amounts of nitrogen in GaAs have drastic electronic effects reducing the bandgap greater than 100 meV per atomic percent of nitrogen. Mixed with InGaAs, long wavelength light emission is possible nearly lattice-matched to GaAs. With a larger conduction band offset than InP, GaInNAs quantum wells on GaAs are thought to have improved thermal properties. Furthermore, being based on GaAs substrates, one can take advantage of well-established processing techniques and a superior Distributed Bragg Reflector (DBR) mirror technology. GaInNAs has shown encouraging characteristics at long wavelengths, including low threshold current densities, high temperature CW operation and high T_0 in the wavelength range of 1.1-1.3 μm [2-4].

However, growing high quality GaInNAs material beyond 1.3 μm has proved challenging. Due to the low solubility of nitrogen in GaAs, nitrogen content needs to be minimized such that phase segregation does not occur. High indium content alloys with dilute nitrogen are then limited in thickness due to a large lattice mismatch. Furthermore, evidence

suggests that high indium GaInNAs tends to phase segregate, thereby drastically reducing non-radiative recombination efficiency. Two solutions exist to improve luminescence output in as-grown high indium GaInNAs. First, by growing tensile strained barriers around compressively strained quantum wells, one can strain compensate and increase the overall thickness of material feasible. Tensile GaNAs barriers can be grown in the active region to allow for an increased number of strained quantum wells increasing optical gain. Second, after thermal annealing as-grown material, photoluminescence sharply improves. However, thermal annealing tends to blue-shift emission and is less effective as wavelength increases. Optical output steadily decreases as wavelength increases, thereby limiting the performance of long wavelength GaInNAs devices.

EXPERIMENTAL DETAILS

GaInNAs/GaNAs/GaAs heterostructures were grown by elemental source molecular beam epitaxy (MBE) on N⁺ and S.I. (001) GaAs substrates. Dimeric arsenic was provided by a thermal cracker and a radio frequency (RF) plasma cell supplied atomic nitrogen. The plasma cell is operated at 250-350 W with a nitrogen gas flow of 0.1-0.5 sccm. Further details have been previously reported [5]. Nitrogen concentration was calibrated using high-resolution X-ray diffraction (HRXRD), electron probe microanalysis (EPMA), secondary ion mass spectroscopy (SIMS), and nuclear reaction analysis Rutherford backscatter spectroscopy (NRA-RBS). A thermal cracker supplied monomeric antimony and the concentration was calibrated using X-ray photoelectron spectroscopy (XPS) and RBS. All PL samples were excited with an Ar⁺ ion laser.

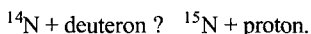
DISCUSSION

It is commonly observed that as-grown GaInNAs has poor luminescent properties. Fortunately, with high temperature anneals of 600-900°C, non-radiative recombination sites are removed and optical emission can be vastly improved. Annealing increases intensity and sharpens peaks but at the same time blue-shifts PL. The precise mechanism for defect removal on anneal is still not well understood. To help understand possible defects contributing to non-radiative recombination, atomic changes during anneal can be separated into two classifications: the reduction of point defects and atomic rearrangement.

Point Defects

Through TEM analysis, dislocation density and other two dimensional defects visible in electron microscopy are extremely low. However, with C-V analysis, deep level defects have been found in GaNAs [6,7]. The origin of these defects is unknown but likely causes include point defects such as trace contaminants, interstitials, vacancies, and antisites. In this research, we have studied interstitials and their possible contribution to the luminescent behavior of GaInNAs using nuclear reaction analysis RBS. In the RBS technique an incident He beam is accelerated at 2.275 MeV toward a thin film of GaInNAs on GaAs. A small fraction of He undergoes a direct collision with the atoms within a few microns and backscatter elastically. The energy of the detected He backscattered from the sample depends on energy lost traveling through the material and the energy lost as a result of the collision itself. Nitrogen, having such a small cross-section with respect to InGaAs, would not be easily resolved. However at certain

energies, the incident ion is absorbed by the nucleus and a variety of particles such as protons are emitted. In this analysis, the following nuclear reaction took place:



The detection of the resulting proton spectrum allows for parts per million sensitivity of nitrogen concentration. In order to study interstitial concentration, He^{++} was channelled down the (100) crystal axis. In this orientation, substitutional atoms have a very low backscattering yield and interstitial atoms are highly visible. Figure 1 shows the NRA-RBS results comparing the channelled versus random crystal orientation. The nitrogen signal, shown on channel 200 is reduced in channelled orientations. Other peaks present close to the nitrogen are surface contaminants such as carbon and oxygen that appear on both random and channelled orientations.

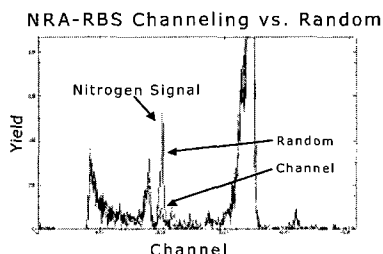


Figure 1. NRA-RBS spectrum of a 150 nm GaInNAs film. The arrows point to the nitrogen peak in both channel and random crystal orientations.

A summary of RBS analysis performed on GaNAs, GaInNAs and GaInNAsSb is shown in table I. In as-grown material, the interstitial concentration is found to be lower than 7%. After thermal anneal interstitial concentration actually increases. Possible explanations for this include a higher equilibrium concentration of interstitials at high temperatures that are quenched when rapidly cooled, or a diffusion of environmental nitrogen present in the annealing chamber into interstitial positions. Due to the low concentration of interstitials and their apparent increase during anneal, it is unlikely that this type of point defect removal is instrumental in the annealing characteristic of GaInNAs.

Vacancies are just one type of point defect effecting luminescence that could be present in GaInNAs. More information about other defects and their origin is currently being studied with other techniques such as C-V, DLTS and low temperature PL.

Table I. Total nitrogen and interstitial nitrogen content on GaNAs, GaInNAs and GaInNAsSb before and after anneal.

	%N	Interstitial %N
GaNAs	2.4	5.8
- Annealed	2.0	8.3
GaInNAs (8%In)	2.4	3.7
- Annealed	2.4	4.2
GaInNAsSb (8%In 7%Sb)	3.0	6.9
- Annealed	3.0	8.2

Atomic Rearrangement

Another possible thermally activated mechanism that could affect luminescent properties in GaInNAs is the diffusion of atoms. There are four types of diffusion that at this stage of analysis seem likely candidates. The first is the diffusion of substitutional nitrogen and the removal from its as-grown location. This has been observed in XRD through a shift of lattice constant in GaNAs films. Also SIMS analysis of GaInNAs has shown an attenuated nitrogen signal after anneal. At first this would seem the most likely candidate to explain the increase in the bandgap on anneal, however other research groups studying this material have not observed similar behavior under their growth conditions. Therefore we can conclude the events which take place during anneal are more complex than just N out-diffusion from quantum wells.

The next three diffusion mechanisms that have been investigated are the phase separation of atoms in the GaInNAs quaternary. Due to unfavorable thermodynamics for solid solubility, under certain conditions diffusion kinetics may allow phase transformations to take place. By growing high nitrogen GaNAs material under varied growth conditions, we have observed nucleation and growth of a GaN rich phase and spinodal decomposition of GaN and GaAs. This only occurs for nitrogen compositions in excess of 5%, however the majority of our material contains a nitrogen concentration less than 3.5%.

A more likely decomposition for dilute nitrogen is the segregation of In and Ga atoms. This is a very common defect in the InGaN system although is not thought to occur in nitrogen free InGaAs. TEM analysis of high In GaInNAs quantum wells however has found In segregation along the length of the wells. Figure 2 shows a low temperature PL spectrum of GaInNAs quantum wells before and after anneal taken at 30K. Two distinct peaks are seen which at higher temperatures are observed as a single peak. If phase segregation is the cause of these double luminescence peaks the diffusion of atoms would occur during growth and not caused by the high temperature anneal. Cathode luminescence (CL) was also performed at 4K on an annealed multiple GaInNAs quantum well sample with emission at 1.23 μm . A very spotty luminescence was observed with features on the order of microns, shown in figure 3. This behavior is more characteristic of InGaN and not typically observed in InGaAs. The optical CL spectrum was very similar to the one found in low temperature PL in figure 2.

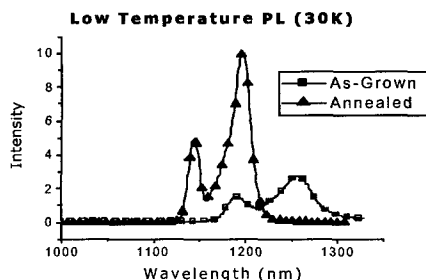


Figure 2. 30K PL of a 3-QW GaInNAs sample, before and after anneal.



Figure 3. 4K CL surface scan of an annealed 3-QW GaInNAs sample with peak emission at 1.23μm.

The last type of atomic rearrangement that is likely to occur is the redistribution of atoms in the lattice, modifying nearest neighbor environments but without long-range phase separation. Two different driving forces and resulting atomic rearrangements have been theorized. One is the minimization of local strain, or the rearrangement of nitrogen toward indium atoms to relax stress in the lattice. The second is the diffusion of nitrogen toward gallium atoms that have lower energy bonds. Both driving forces may play a role in the reordering of atoms within the GaInNAs quaternary. By changing the overall bonding energy and strain in the system, bandgap shifts would be likely and this could explain the blue-shift of luminescence on anneal. This type of atomic rearrangement is current being investigated.

Strain Compensation

The concentration of nitrogen in GaInNAs is currently limited to under 4% with current growth techniques. Therefore, in order to extend this material to longer wavelengths, one must increase the amount of indium, compressively straining the material. While this is known to be beneficial for optical devices, the formation of dislocations will occur if the critical thickness is exceeded. This limits the number of quantum wells that can be grown and would reduce the

maximum output power of lasers and prevent its use in some modulator structures. Instead of surrounding our quantum wells with GaAs, we have begun using tensile-strained GaNAs barriers. By offsetting the compressive stress generated by our strained quantum wells, many more quantum wells can be grown with a total thickness much larger than the inherent critical thickness for dislocations. Furthermore, by surrounding our quantum wells with GaNAs, longer wavelength devices are possible. The GaNAs barriers have a larger concentration of nitrogen than the quantum wells, therefore, out-diffusion of nitrogen from the wells into the surrounding environment is reduced. Also the band offsets between the barrier and well is reduced, thereby lowering the confinement energy further red-shifting wavelength emission. Overall confinement of carriers is not reduced since GaAs is grown away from the quantum wells inhibiting carrier diffusion at the GaNAs-GaAs interface.

A nine quantum well device of highly strained 30% In, 3.3% N GaInNAs active material and GaNAs barriers has been grown dislocation free and is shown in figure 4. The resulting PL spectrum of 3, 6 and 9 quantum well structures is also shown. When we increased from 3 to 6 quantum wells, luminescence increased 2.4 times, and from 3 to 9 wells, PL increased 3.9 times. The total thickness of strained active material for the 9 quantum well sample was 63 nm, much greater than the critical thickness. A 30% InGaAs sample is known to have a critical thickness of under 10 nm. By growing tensile-strained GaNAs, a much larger active medium can be present greatly increasing optical gain in grown devices.

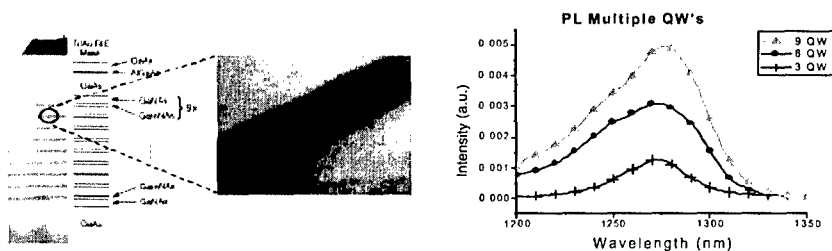


Figure 4. TEM (left) of 9 QW GaInNAs sample, and PL spectrum of 3, 6 and 9 QW GaInNAs samples (right).

GaInNAs/GaNAs Ridge Waveguide Laser Diodes

In-plane laser diodes were grown and fabricated with 32% In, 2.5% N GaInNAs active material, and 3.5% N GaNAs barriers. A ridge waveguide structure was fabricated and tested. The optical spectrum, I-V, and L-I are shown in figure 5. The optical spectrum was acquired at 1.2 times the threshold current with a 1ms pulse period and a 0.1% duty cycle. The laser output was at 1.31 μm , with a current threshold density of 1.5 kA/cm^2 . A differential quantum efficiency of 0.45 W/A was measured. The laser diodes that were tested were not anti-reflection or high-reflection coated. Laser operation was found to occur as high as 90°C.

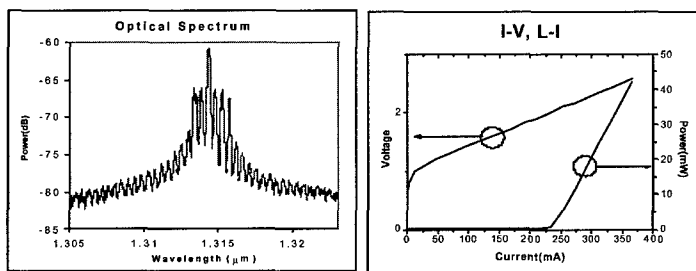


Figure 5. Optical spectrum (left) and I-V, L-I (right) of a GaInNAs/GaNAs 3-QW ridge-waveguide in-plane laser.

GaInNAsSb

As more nitrogen and indium is added into GaAs, it becomes increasingly difficult to maintain a solid solution alloy. Surface energy and high surface diffusivity plays an important role in the way atoms incorporate in the bulk. Once confined to the solid, bulk diffusivity is much lower than at the surface, thus a solid solution can be maintained during anneal. A surfactant has the ability to reduce surface energy and enhance soluble incorporation at the surface of a growing material. Antimony is a well-known surfactant aiding the incorporation of In within GaAs. A thermal cracking effusion cell provides a source of Sb during GaInNAs growth. A careful calibration of Sb growth rate and sticking coefficients in GaInNAs has not yet been completed, so for the following analysis only Sb flux has been reported.

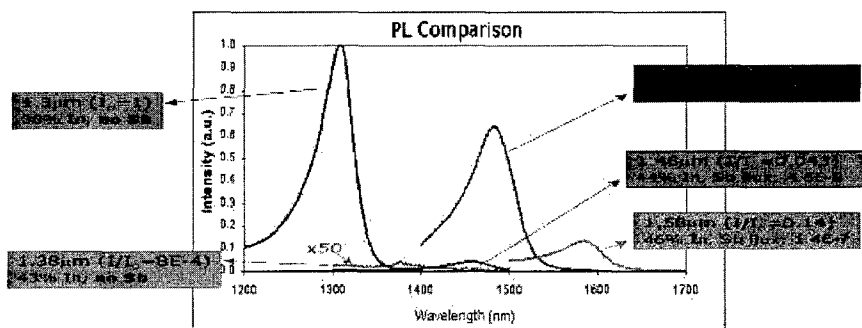


Figure 6. PL spectrum of GaInNAs and GaInNAsSb 3-QW samples, all with 2.5% N. From left to right: 1.3 μm , 38% In, Int.=1; 1.38 μm , 43% In, Int.=0.0008; 1.46 μm , 44% In, 4.6×10^{-8} torr Sb, Int.=0.043; 1.48 μm , 45% In, 7.2×10^{-8} torr Sb, Int.=0.65; 1.58 μm , 46% In, 1.4×10^{-7} torr Sb, Int.=0.14.

Figure 6 plots five different PL spectrum two without the use the Sb and three with Sb present for the entire GaInNAs/GaNAs active region growth. The leftmost, highest intensity spectrum is a 1.3 μm 38% In, 2.5% N, GaInNAs/GaNAs 3 quantum well structure with its

intensity normalized to unity. By increasing the In to 42%, 1.38 μm is measured, however the intensity is reduced over 1000 times. In the next three spectra, increased Sb was added to relatively the same GaInNAs composition. The structure of these PL samples was three GaInNAsSb quantum wells surrounded by GaNAsSb barriers. Wavelength operation was changed from 1.46 to 1.58 μm with the highest efficiency material showing a wavelength of 1.48 μm . This material had a PL intensity that was 65% of the highest intensity 1.3 μm material grown compared with 0.08% for shorter wavelength material grown without antimony. Antimony incorporation has been measured using X-ray photoelectron spectroscopy (XPS) and RBS in quantities as high as 7% in these materials, but careful calibration has not been performed. The exact mechanism for improving luminescence and red-shifting output is currently unknown. Antimony seems to be acting as both a surfactant and a significant alloy constituent improving optical emission and enabling wavelength operation as long as 1.6 μm . Table I indicates a difference in N composition with the presence of Sb. Both the increase of nitrogen content and the presence of antimony can be responsible for the longer wavelength PL shift.

Laser devices were also grown and fabricated with 44% In, 2.5% N GaInNAsSb quantum wells and GaNAsSb barriers. A flux of 6.89×10^{-8} torr of Sb was used during barrier and well growth. This flux has been measured to incorporate about 7% Sb into GaInNAs. The optical spectrum and L-I plot is shown in figure 7. A peak wavelength of 1.464 μm was taken at 1.2 times threshold. A threshold current density of 2.8 kA/cm^2 was measured for the devices with a width of 5 μm and length of a 1.3 mm. The measurements were taken with a pulsed current source at room temperature.

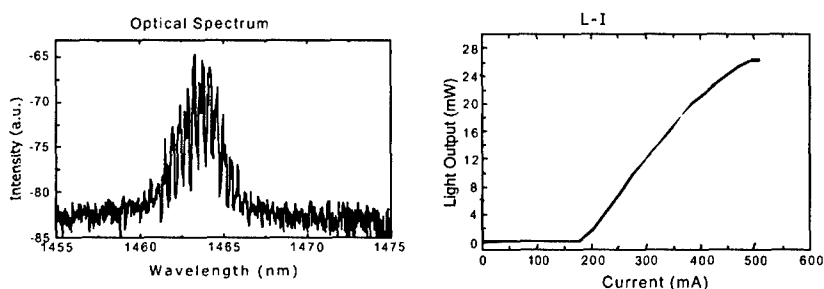


Figure 7. Optical Spectrum (left) and L-I (right) of a GaInNAsSb/GaNAsSb 3-QW ridge-waveguide device.

CONCLUSIONS

As-grown GaInNAs typically has poor optical properties due to defects incorporated during growth. Thermal anneal removes these defects but blue-shifts optical emission. This paper discusses likely defects responsible for this behavior. A new barrier structure made of tensile-strained GaNAs has been grown. These barriers increase wavelength and strain compensate compressive quantum wells. With these barriers, increased quantum well high-power lasers and modulators are now possible. A new material, GaInNAsSb, is also presented. Antimony acts as both a surfactant improving luminescence at long wavelengths and an alloy

constituent, further red shifting emission. High efficiency PL, as long as 1.6 μm , has been demonstrated. Finally, two laser structures GaInNAs/GaNAs and GaInNAsSb/GaNAsSb are shown. With low thresholds and high output powers, it further substantiates this material system's potential as a replacement for 1.3-1.55 μm opto-electronic devices.

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